

3D Electron Diffraction Study of Delithiation Induced Lattice Distortion in Li-rich Layered Oxide Cathode

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Li-rich Mn-based materials, which is composed of a layered rhombohedral LiTMO₂ (TM = Ni, Co, Mn) component and a monoclinic Li₂MnO₃ component, showing a high specific capacity (> 250 mAh g⁻¹). In contrast to the conventional LiTMO₂ materials, the higher capacity stems from the extra activation of the Li₂MnO₃ component with partially reversible oxygen redox above 4.5 V, whereas it also brings some fatal drawbacks. Voltage decay and hysteresis result in the continuous capacity loss and restrict its large-scale commercial applications. At present, the in-depth mechanism of performance decay and its relationship with structural evolution are still poorly understood [1].

Ideally, Li⁺ ions are reversibly migrated into and out of the framework of layered materials under the driving of voltage. However, in actual, uneven Li⁺ (de)intercalation and heterogeneous electrochemical reactions are often occurred in these process, causing nonequilibrium structural dynamics at both the macroscopic and microscopic level. This is thought to be the origin of mechanic strain and failure of cathode particles. In this study, we carefully investigated the structural changes of the first charged Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O₂ (LMR) particles by aberration-corrected high-resolution TEM (HRTEM) and three-dimensional electron diffraction (3D-ED) techniques.

Figure 1a shows the low-magnification TEM image of the charged LMR particle, which indicates obvious stacking defects on the surface. 3D-ED technique has been shown to quickly and automatically collect structural information on a large scale and easily interpret local structural defects in a three-dimensional space. Hence, it was first used for the structural characterization of particle. As exhibited in **Figure 1c**, the arc-like reflections suggest the lattice bent along the layered stacking direction. The further HRTEM observation (**Figure 1d**) indicated the surface lattice is distorted and deformed significantly, which means that surface occurred more violent electrochemical oxidation and Li⁺ ion deintercalation. The corresponding fast Fourier transform (FFT) pattern (**Figure 1e**) present streaked reflection, demonstrating the stacking faults of layered structure. Besides, FFT also exhibited the existence of spinel phase in the charged LMR.

In summary, it is confirmed that structural deformation and phase transition first occur on the particle surface owing to inhomogeneous Li⁺ deintercalation at the early stages of the electrochemical process. It is believed that they will expand into the interior of the material to cause performance failure in subsequent electrochemical cycles [2].

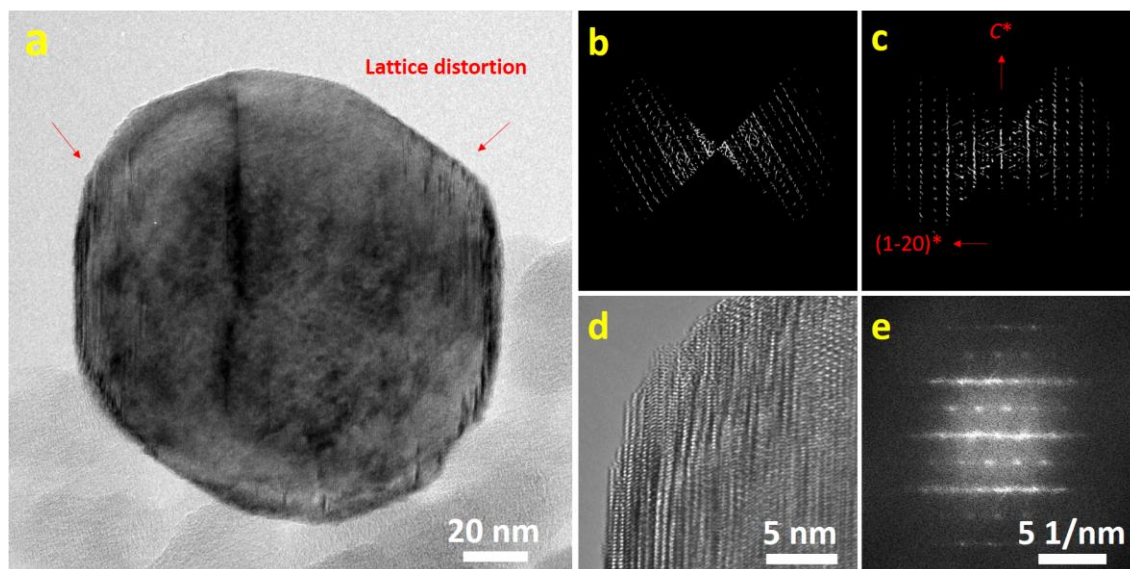


Figure 1. (a) Low-magnification TEM image of first charged LMR particle. (b and c) The projections of the reconstructed reciprocal lattice. (d) HRTEM image of the charged LMR particle surface and (e) corresponding FFT pattern.

References:

[1] L. Yu, T. Liu, R. Amine, J. Wen, J. Lu and K. Amine, *ACS Appl. Mater. Interfaces*, 2022, DOI: 10.1021/acscami.1c22091.

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